Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 2427–2430
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Fabrication of β-Si_3N_4 whiskers from a GPSed-RBSN sponge using $6Y_2O_3$–2MgO additives

Do-Van Tuyen [a], Jeong-Ho Yoo [b], Hai-Doo Kim [c], Byong-Taek Lee [a,*]

[a] Department of Biomedical Engineering and Materials, Soonchunhyang University, 366-1, Ssangyong-dong, Cheonan, Chungnam 330-090, South Korea
[b] National Nanofab Center, 355 Gwahakno, Yuseong-Gu, Daejeon City, South Korea
[c] Ceramic Materials Group, Korea Institute of Materials Science, Changwon, Kyungnam 641-010, South Korea

Received 18 March 2010; received in revised form 30 March 2010; accepted 27 June 2010
Available online 4 August 2010

Abstract

In this study, β-Si_3N_4 whiskers with a diameter of 0.05–1.5 μm and length of about 70 μm were successfully fabricated using a gas pressure sintered (GPSed)-reaction boned silicon nitride (RBSN) process at 1550 °C for 9 h. The β-Si_3N_4 whiskers grew on the frame and filled fully in the pores of the GPSed-RBSN sponge. $6Y_2O_3$–2MgO additives played a significant role in the growth of β-Si_3N_4 whiskers and α-Si_3N_4 whiskers, while α-Si_3N_4 whiskers, which were grown inside the RBSN sponge through the vapor–solid mechanism, had a diameter ranging from 50 to 100 nm and length of about 80 μm.

Keywords: B. Whisker; Silicon nitride; GPSed-RBSN

1. Introduction

Silicon nitride (Si_3N_4) whisker-based materials have received considerable attention in recent years due to their desirable engineering properties such as light weight, chemical stability, good resistance to thermal shock and oxidation [1,2]. Previously, they have been used as reinforced materials for light metals, ceramic-matrix composites, metal matrix composites and plastics [3,4]. It was reported that the use of Si_3N_4 whiskers as reinforcement for Al composites provided even higher tensile strength and better machinability than SiC whisker reinforcement [4], even though SiC whiskers have been the most extensively examined type of ceramic whiskers [5]. Some researchers have recently shown that the high fracture toughness can be improved with larger and longer β-Si_3N_4 grains [6,7]. In addition, ceramic β-Si_3N_4 whiskers that had a diameter of about 1 μm and length of 10–20 μm, which were used to reinforce aluminum alloy composites, exhibited high tensile strength at room and high temperatures [8].

It has been shown that Si_3N_4 whiskers can be produced by carbon thermal reduction of silica based materials [9], chemical vapor deposition method [10] and combustion synthesis from Si_3N_4 powders directly [11]. To date, there have been no reports on the formation of β-Si_3N_4 whiskers using Si powder with $6Y_2O_3$–2MgO as additives coated on a polyurethane sponge, through the gas pressure sintered reaction-bonded silicon nitride (GPSed-RBSN) technique despite the fact that this process has been used to evaluate GPSed-RBSN bodies [12,13]. However, in our previous report, we demonstrated that fine rod-like β-Si_3N_4 structures with a high aspect ratio could be formed in a porous body using $6Y_2O_3$–2MgO as additives [14].

In this investigation, we attempted to develop β-Si_3N_4 whiskers with a high aspect ratio in a Si_3N_4 ceramic sponge. In addition, the effect of $6Y_2O_3$–2MgO additives on the formation of β-Si_3N_4 whiskers was investigated.

2. Experimental procedure

Si powder (Permascand, Sweden, average size: 7 μm) in combination with a polymer sponge (average pore size diameter: 300 μm, Customs Sponge Ltd., UK) was used as

* Corresponding author. Tel.: +82 41 570 2427; fax: +82 41 577 2415.
E-mail address: lbt@sch.ac.kr (B.-T. Lee).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.07.011

the pore-forming agent. Additives, 6 wt.% Y_2O_3 (purity > 99.99%, Aldrich, USA) and 2 wt.% MgO (purity 99.99%, Aldrich, USA) were mixed with 92 wt.% Si powders to create a mixture of powder using a wet ball mill in alcohol for 24 h with Si_3N_4 ball as the milling media. The slurry was separated from the milling media and dried on a hot plate while stirring. The mixture was then kept in the oven at 80 °C for 24 h. Twenty grams of the powder mixture was then stirred vigorously in 70 ml of alcohol for 4 h to produce the slurry. As a binder, 4 g of poly ethylene glycol (PEG) was dissolved in 30 ml alcohol in another beaker for 3 h, which was subsequently added to the slurry and stirred for 12 h. The polyurethane sponge templates were cut carefully into the appropriate dimensions and uniformly immersed in the slurry throughout the sponge without blocking the pores. These dipping and drying steps were repeated four times. The sponges were then dried at 80 °C for 12 h and heat treated to burn out the binders and the polymer sponges at 600 °C for 3 h in air. Then, nitridation of the Si substrate was carried out at 1400 °C for 2 h while flowing a N_2 + 10% H_2 gas mixture at a pressure of 0.5 MPa. Finally, the Si_3N_4 sponges were sintered at 1550 °C for 9 h using gas pressure sintering (GPS).

The morphology of the Si_3N_4 whiskers in the porous Si_3N_4 ceramic sponge was investigated using transmission electron microscopy (TEM) and high-revolution transmission electron microscopy (HRTEM) techniques. A field emission scanning electron microscope (SEM, Hitachi S4000, Hitachi Instruments Inc., CA) equipped with an energy-dispersive X-ray spectrometer (EDS) was used to characterize the image and the composition of the samples produced in the experiments. X-ray diffraction (XRD, Siemens X-ray diffractometer, D-500, graphite monochromator) was also employed to determine the crystal phase.

3. Results and discussion

Fig. 1 shows low magnification SEM micrographs of the polymer sponge, which was coated with the Si slurry. The thickness of the sponge frame was about 70 μm as shown by the arrowheads in Fig. 1(a). Fig. 1(b) shows the Si_3N_4 body after nitridation at 1400 °C for 2 h. Large pores with a size of about 300 μm were observed in both cases as shown in Fig. 1 (a) and (b). In addition, the Si_3N_4 whiskers fully grew inside the specimen (Fig. 1(b)). A higher magnification SEM micrograph of the Si_3N_4 whiskers (Fig. 1(c)) was taken from the pore shown in the dotted circle in Fig. 1(b). As shown in this higher magnification image, most of the whiskers inside the pores had a length of about 80 μm. The EDS profile of the whiskers (marked P in Fig. 1(c)) was measured to confirm that the formed whiskers mainly consisted of silicon and nitrogen elements (Fig. 1(d)).

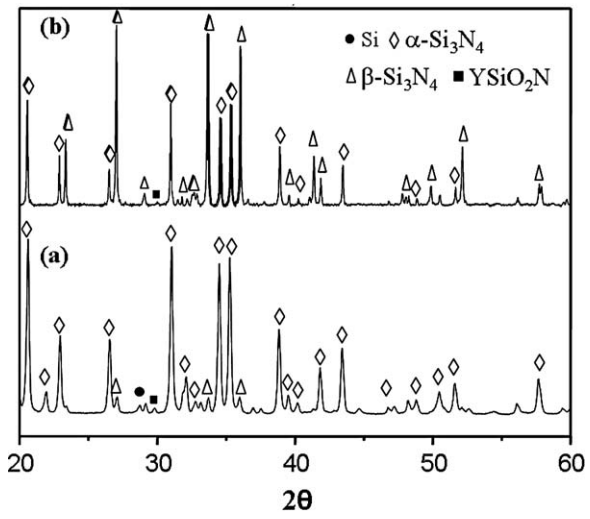

Fig. 2. XRD profiles of the porous Si_3N_4 ceramic sponge (a) nitrided at 1400 °C for 2 h and (b) sintered at 1550 °C for 9 h, respectively.

Fig. 2 shows the XRD profiles of the Si_3N_4 bodies, which were nitrided at 1400 °C for 2 h (a) and sintered at 1550 °C for 9 h (b), respectively. Residual Si and $YSiO_2N$ as weak peaks were detected with the main α-Si_3N_4 peaks, and minor β-Si_3N_4 peaks as shown in Fig. 2(a). As sintered at 1550 °C for 9 h, the main β-Si_3N_4 and minor α-Si_3N_4 phases were observed with the secondary phase, while, no Si peak was observed in the XRD profile as shown in Fig. 2(b). The formation of this crystalline secondary phase was reported by Zhu et al. [15]. On the other hand, no crystalline secondary phase containing Mg was detected by XRD. This can be explained by the fact that MgO takes part in the formation of

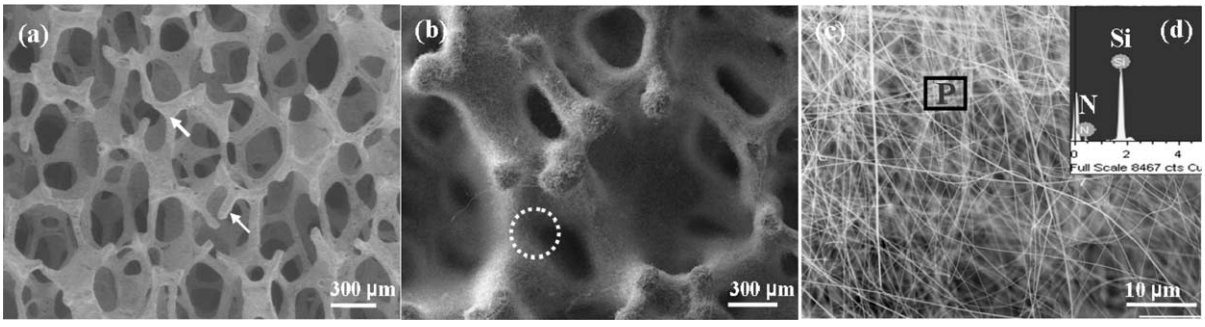

Fig. 1. Low magnification of SEM micrographs of Si_3N_4 sponge (a) before and (b) after nitridation, (c) high magnification of Si_3N_4 whiskers, and (d) EDS profile of Si_3N_4 whiskers.

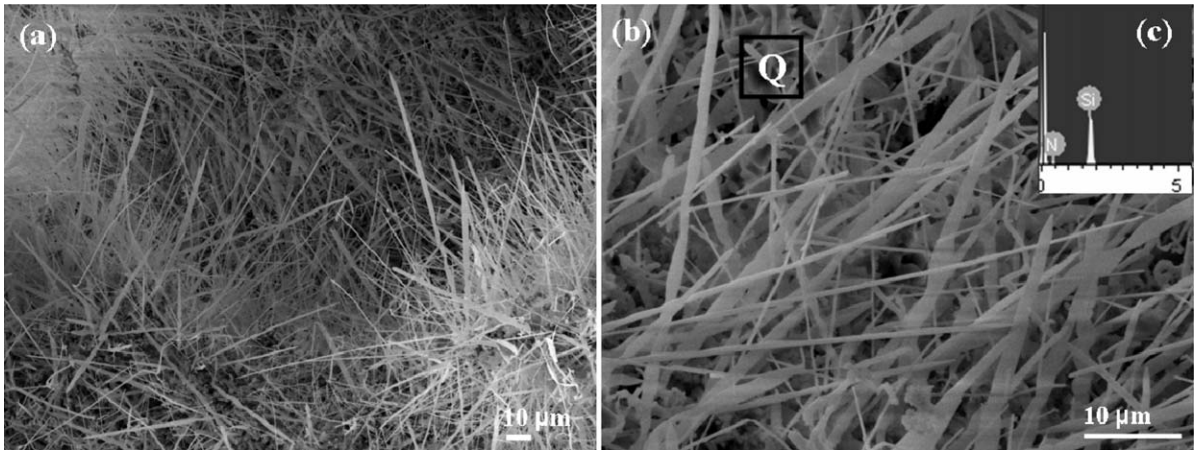

Fig. 3. (a) Low and (b) enlarged SEM micrographs porous Si_3N_4 whiskers sintered at 1550 °C for 9 h.

a liquid phase to form an amorphous phase, which accelerates the α-Si_3N_4 to β-Si_3N_4 transformation and crystal growth. This same phenomena has also been observed for Al_2O_3 [16].

Fig. 3 shows low and high magnification SEM micrographs and the EDS profile of the Si_3N_4 whiskers. Large numbers of network type Si_3N_4 whiskers were observed on the scaffold frame with lengths of approximately 70 μm, as shown by the arrows in Fig. 1. From the enlarged image shown in Fig. 3(b), it is clear that the diameter of the Si_3N_4 whiskers ranged from 0.5 to 1.5 μm. The EDS profile of the whiskers marked Q in Fig. 3(b) was measured to confirm that the Si_3N_4 whiskers mainly consisted of silicon and nitrogen elements (Fig. 3(c)). There is no evidence indicating that the tips of the whiskers are in a droplet form, suggesting that the growth of the whiskers may take place through the vapor–solid (VS) mechanism [17,18]. This indicates that the formation of the Si_3N_4 whiskers was due to the vapor phase reaction between the intermediate SiO phase and N_2 during the nitridation process. We have previously reported on the formation of the SiO phase [13]. Larger Si_3N_4 whiskers were formed when the samples were sintered at 1550 °C for 9 h. This may have occurred because the Si (1410 °C) powder formed a

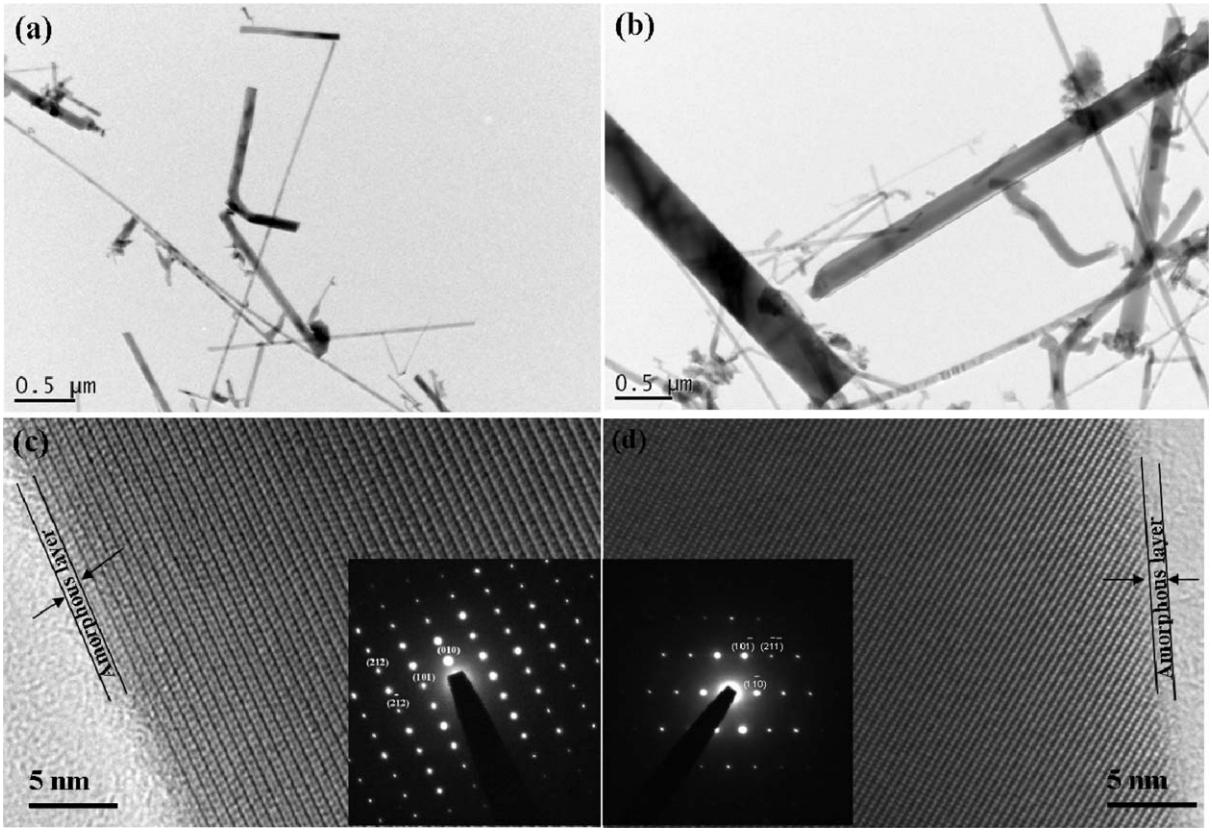

Fig. 4. TEM, HRTEM, and the electron diffraction pattern (a–c) nitrided at 1400 °C and (d–f) sintered at 1500 °C, respectively.

more suitable solvent for Si_3N_4 whiskers and assisted in the α-Si_3N_4 to β-Si_3N_4 phase transformation [19]. Furthermore, since the lowest eutectic temperature of the Si_3N_4–SiO_2–Y_2O_3–MgO does not exceed 1350 °C [15], the Y–Si–O–N liquid phase may also have accelerated the α-Si_3N_4 to β-Si_3N_4 transformation and crystal growth.

Fig. 4 shows TEM, HRTEM, and the electron diffraction pattern of the Si_3N_4 whiskers (a and c) nitrided at 1400 °C for 2 h, and (b and d) sintered at 1550 °C for 9 h. Si_3N_4 whiskers having diameters of about 50–100 nm are shown in Fig. 4(b). The HRTEM image was acquired from the zone axis of the $[1\,0\,\bar{1}]$ α-Si_3N_4 whiskers and showed highly crystalline Si_3N_4 whisker with an amorphous layer that had a thickness of about 1 nm (Fig. 4(c)). Furthermore, the electron diffraction pattern, which was taken from the center of the Si_3N_4 whiskers is shown in the insert in Fig. 4(c), shows that the spacing distances between two adjacent fringes in the (0 1 0), (1 0 1), and $(2\,\bar{1}\,2)$ planes were 0.670 nm, 4.90 nm, and 2.27 nm, respectively. These spacing distances demonstrate that the whiskers have the characteristic features of α-Si_3N_4. The diameter of the Si_3N_4 whiskers sintered at 1550 °C for 9 h ranged from approximately 50 nm to 500 nm as shown in Fig. 4(b). The HRTEM image was acquired from the [1 1 1] zone axis of the Si_3N_4 whiskers and shows highly crystalline Si_3N_4 whiskers even though their surface was coated with a thin amorphous layer less than about 1 nm thick (Fig. 4(d)). Moreover, the electron diffraction pattern, which is shown in the insert in Fig. 4(d), shows that the spacing distances between two adjacent fringes in the $(1\,\bar{1}\,0)$, $(1\,0\,\bar{1})$, and $(2\,\bar{1}\,\bar{1})$ planes were 3.8 nm, 2.64 nm, and 1.89 nm, respectively. These spacing distances demonstrate that the Si_3N_4 whiskers have the characteristic features of β-Si_3N_4.

4. Conclusions

β-Si_3N_4 whiskers were successfully fabricated using the GPSed-RBSN process with $6Y_2O_3$–2MgO as additives. Whiskers with diameter of about 0.05–1.5 μm and length of about 70 μm were obtained. In the nitridation stage, the electron diffraction pattern images indicate that the Si_3N_4 whiskers were α-Si_3N_4 and the growth of whiskers follows the vapor–solid (VS) mechanism. The combined results of this study demonstrate that the use of GPSed-RBSN with $6Y_2O_3$–2MgO as additives is an effective method to prepare elongated β-Si_3N_4 whiskers.

References

[1] I.C. Jung, S.H. Cho, S.W. Na, J. Lee, H.S. Lee, W.S. Cho, Synthesis of Si_3N_4 whiskers in porous SiC bodies, Mater. Lett. 61 (2007) 4843–4846.

[2] A.H. Feng, L. Geng, J. Zhang, C.K. Yao, Hot compressive deformation behavior of a eutectic Al–Si alloy based composite reinforced with α-Si_3N_4 whiskeer, Mater. Chem. Phys. 82 (2003) 618–621.

[3] K. Kijima, N. Setaka, H. Tanaka, Preparation of silicon nitride single crystals by chemical vapor deposition, J. Cryst. Growth 24–25 (1974) 183–187.

[4] H. Matsubara, Y. Nishida, M. Yamada, L. Shirayanagi, T. Imai, J. Mater. Sci. Lett. 6 (1987) 1313.

[5] S.R. Nutt, Microstructure and growth model for Rice–Hull-derived SiC whiskers, J. Am. Ceram. Soc. 71 (1988) 149–156.

[6] P. Sajgalik, J. Dusza, Reinforcement of silicon nitride ceramics by β-Si_3N_4 whiskers, J. Eur. Ceram. Soc. 5 (1989) 321–326.

[7] K. Hirao, T. Nagaoka, M.E. Brito, S. Kanzaki, Microstructure control of silicon nitride by seeding with rod-like, J. Am. Ceram. Soc. 77 (1994) 1857–1862.

[8] I. Tochigi, T. Imai, Kyosuke, Scripta Metall. Mater. 32 (1995) p.1801–1806.

[9] S. Shimada, T. Kataoka, Separate growth of α-Si_3N_4 and β-Si_3N_4 whiskers on or near a carbon substrate by carbothermal reduction, J. Am. Ceram. Soc. 84 (2001) 2442–2444.

[10] C. Kawai, A. Yamakawa, Crystal growth of silicon nitride whiskers through a VLS mechanism using SiO_2–Al_2O_3–Y_2O_3 oxides as liquid phase, Ceram. Int. 24 (1998) 135–138.

[11] Y.G. Cao, H. Chen, J.T. Li, C.C. Ge, S.Y. Tang, J.X. Tang, X. Chen, Formation of α-Si_3N_4 whiskers with addition of NaN_3 as catalyst, J. Cryst. Growth 234 (2002) 9–11.

[12] B.T. Lee, J.H. Yoo, H.D. Kim, Size effect of raw Si powder on microstructures and mechanical properties of RBSN and GPSed-RBSN bodies, Mater. Sci. Eng. A 333 (2002) 306–313.

[13] B.T. Lee, J.H. Yoo, H.D. Kim, Nitridation mechanism of Si compacts studied by transmission electron microscopy, Mater. Trans. JIM 37 (1996) 1547–1553.

[14] D.V. Tuyen, Y.J. Park, H.D. Kim, B.T. Lee, Formation of rod-like Si_3N_4 grains in porous SRBSN bodies using $6Y_2O_3$–2MgO sintering additives, Ceram. Int. 35 (2009) 2305–2310.

[15] X. Zhu, Y. Zhou, K. Hirao, Effects of processing method and additive composition on microstructure and thermal conductivity of Si_3N_4 ceramics, J. Eur. Ceram. Soc. 26 (2006) 711–718.

[16] L.K.L. Falk, R. Pompe, G.L. Bunlop, Development of microstructure during the fabrication of Si_3N_4 by nitridation and pressureless sintering of Si: Si_3N_4 compacts, J. Mater. Sci. 20 (1985) 3545–3556.

[17] Y. Luo, Z. Zheng, Z. Xie, Z. Zhang, Growth of silicon nitride whisker from polytitanosilazane, Mater. Lett. 58 (2004) 2114–2117.

[18] Y. Xu, C. Cao, H. Du, J. Li, H. Zhu, Synthesis and photoluminescence of belt-shaped Si_3N_4 whiskers, Mater. Lett. 61 (2007) 3855–3858.

[19] A.S. Mukasyan, V.M. Martynenko, A.G. Merzhanov, I.P. Borovinskaya, Y.M. Blinov, Combust. Explos. Shock Waves 22 (1986) 534 (Engl. Transl.).